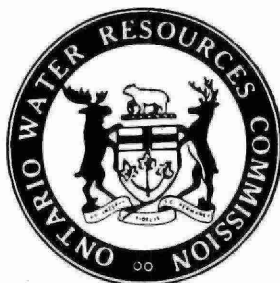


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REMOVAL OF HYDROGEN SULPHIDE FROM GROUND WATER



DIVISION OF RESEARCH

ONTARIO WATER RESOURCES COMMISSION

April, 1969

R. P. 2022

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REMOVAL OF HYDROGEN SULPHIDE FROM GROUND WATER

By:

A. V. Giffen

April, 1969

Division of Research
Paper No. 2022

A. J. Harris
Director

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Chairman

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General Manager

The Ontario Water Resources Commission

SUMMARY

Well water containing concentrations of hydrogen sulphide can be treated by aeration or by combined pH reduction and aeration. These methods, however, do not completely remove the hydrogen sulphide. If it is desired to reduce the sulphide level to zero, chemical treatment is required, regardless of whether aeration alone or a combination of pH reduction and aeration is used.

Complete removal of low concentrations of hydrogen sulphide (less than 8 ppm) can be best accomplished by means of chlorination. For higher concentrations, a combined aeration-chlorination treatment should be used. When chlorine is used, it not only oxidizes but also chlorinates, and, in most cases, the chloro-derivatives which are formed are more objectionable than the original taste and odour producing compounds.

Potassium permanganate may be effectively used to remove concentrations of hydrogen sulphide below 2.5 ppm. As an alternative, it is odourless and when applied as a solution, it can be readily controlled by a visual technique.

REMOVAL OF HYDROGEN SULPHIDE FROM GROUND WATER

INTRODUCTION

Many ground water supplies contain quantities of hydrogen sulphide (H_2S) that cause them to be unsatisfactory for domestic use without treatment. The H_2S in ground water is produced by reduction of sulphates, iron pyrites or decomposition of organic matter and is likely to be found in water that has percolated through beds of lignite or other organic remains. Its disagreeable rotten-egg odour makes it highly objectionable in very small amounts. It is also corrosive to metals but is not injurious to persons drinking water having the amounts generally encountered.

METHODS OF REMOVAL

There are several methods of treatment that could be used for the removal of sulphides in water supplies. Since sulphides may be present in the form of both metallic sulphides and gaseous hydrogen sulphide, it may be necessary to utilize mechanical and chemical processes in order to achieve complete removal.

Aeration

The removal or reduction of H_2S by aeration is mostly mechanical as, at the temperatures involved, the oxidation of the H_2S is negligible. Three general types of aerators in use are:

1. Spray aeration - water under pressure is forced into the air through spray nozzles or fountains as a very fine spray or droplets.
2. Forced-draft aeration - thin sheets of water fall over a series of wood baffles for a predetermined height.
3. Air diffusion - air under pressure is forced up through a solid body of water in very fine bubbles, thereby exposing a large surface area to the air.

H_2S is poisonous when inhaled and atmospheres containing more than 20 ppm should be avoided for exposures of over 8 hours, while concentrations of 600 to 800 ppm will cause acute poisoning in a short time. It has been demonstrated

that concentrations of sulphides, expressed as H_2S , from 5 to 20 ppm are extremely objectionable when the gas is discharged to the atmosphere as a result of aeration.⁽¹⁾ Therefore, in aerating to remove this gas, it should be dissipated into the atmosphere with minimum risk of exposure to humans and animals.

Aeration alone, when sufficient capacity is provided, can reduce the sulphides, even when present in appreciable concentrations, to below 2 ppm (Appendix B). However, in alkaline waters, H_2S removal by aeration may be difficult because the sulphides are present in the water mostly as metallic salts. Data in Table I show the relationship of pH and percentages of total sulphides available as H_2S .

TABLE I

<u>Percentage of Total Sulphide Present as H_2S</u> ⁽²⁾	
<u>pH Value</u>	<u>Percent H_2S</u>
5.0	98
6.0	83
7.0	33
7.5	14
8.0	4.8
8.6	1.2
9.0	0.5

The decrease in the pH value shifts the ionization constant, and, as a result of the new equilibrium, a larger percentage of the total sulphides is converted to H_2S , which is more readily removed by aeration. This principle has led to the use of mineral acids or carbon dioxide (CO_2) to reduce the pH value prior to, or during, aeration.⁽¹⁾

To effect sulphide removal by pH reduction, the pH value should be between 4 and 5 for optimum or most efficient results. A major disadvantage of this method of treatment is that some adjustment must be made in the pH value of the water after treatment.

It is suspected that the H_2S concentrations reported in Appendix A may not accurately describe the H_2S levels experienced in the ground waters found in Russell County. The Hach Kit analyzer as used, tests for soluble sulphides only, and will not detect insoluble forms (e.g. FeS). The test is carried out by filling a sample bottle to the mark with the water sample. The H_2S in the water is aerated out of the water by the addition of an effervescent tablet (an Alka-Seltzer tablet) to the water sample and the gas evolved is made to pass through a disk of H_2S sensitive paper inside the cap of the test bottle. This causes the paper to colour,

depending upon the amount present. The colour is then compared with a colour chart to determine the parts per million H_2S present. The range of this test is 0.1-5 ppm H_2S .⁽³⁾

Referring to Table I, with the pH value between 7.0 and 8.6 (the range reported in Appendix A), only 33 and 1.2 percent of the total sulphides will be present as H_2S . Generally, this will be the fraction measured by the Hach Kit. The undetected insoluble forms then, could range as high as 50-100 ppm, expressed as H_2S . This discrepancy will affect the selection of the most practical treatment method.

Chlorination

It is practically impossible to completely remove H_2S by aeration, and oxidation with chemicals is frequently relied upon to complete its elimination.⁽¹⁾

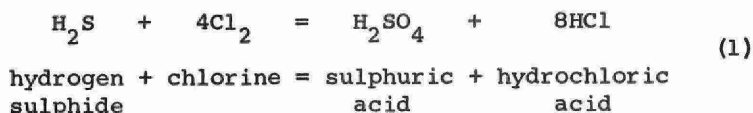
When the concentration of H_2S is less than 8 ppm, the chlorination-filtration treatment is the most satisfactory method (Appendix C-1). A chemical feeder automatically adds chlorine to the water, preferably down the well at the end of the pump drop pipe or at least before the pump. The chlorine oxidizes the H_2S eliminating the bad odour and corrosion problems, and also kills any sulphur bacteria present.

Following chlorination, the water for most purposes is passed through a sediment filter to remove the precipitated sulphur (Appendix C-2). To ensure complete precipitation of the sulphides and to allow for variations in H_2S which may occur in the water supply, the chemical feeder is usually set to maintain a reasonably high chlorine residual in the treated water. To remove the objectionable chlorine taste and odour, dechlorination of small quantities of water for drinking and cooking purposes can be accomplished by installing a small activated carbon filter, on a tap in the kitchen for example.⁽⁴⁾ A large carbon filter could be installed to dechlorinate the whole water supply; normally, however, it is not likely that the added cost of dechlorinating the whole supply can be justified (Appendix C-3).

Aeration-Chlorination

For higher concentrations of H_2S , a combined aeration-chlorination-filtration treatment is the best method for the removal of H_2S from well water.

Equation (1) shows the results of a reaction using chlorine to oxidize hydrogen sulphide. In this reaction, theoretically, 8.4 ppm of chlorine are required to remove each ppm of H_2S . The large quantities of chlorine that are



needed for a complete removal of high concentrations of H_2S would help to increase the cost of treatment. Consequently, for these water supplies, a more economical method is to remove as much hydrogen sulphide as possible by aeration and then utilize chlorination for complete removal.

Potassium Permanganate

When chlorine is used for the oxidation of impurities, it not only oxidizes but also chlorinates, and, in most cases, the chloro-derivatives which are formed are more objectionable than the original taste- and odour-producing compounds.⁽⁵⁾

Potassium permanganate is a strong oxidant which has been used to oxidize odour-producing compounds (Appendix D). Dry, or in solution, it is odourless, noncorrosive and it does not produce harmful vapours. It can be handled by conventional methods and can be fed by a standard chemical solution feeder. Because KMnO_4 is not compatible with rubber, any pump diaphragm or hose line should be made of plastic. Metallic pipe lines are entirely satisfactory for transporting permanganate solution.

Potassium permanganate when applied as a solution from a solution feeder is very easy to control. The time required for the optimum dose of KMnO_4 to oxidize the H_2S varies from one water supply to the next. Generally, 10-15 seconds will be sufficient to achieve almost complete oxidation.

Dosages can be readily controlled by a visual technique. A very slight pink colour denotes that the concentration of KMnO_4 (excess) is approximately 0.05 ppm.

Following treatment, the water for most purposes is passed through a special filter to remove the excess permanganate and precipitated sulphur. The filter looks like a water softener, but the tank contains Manganese (Mn) Green Sand, an oxidizing agent, which oxidizes the excess permanganate and collects the flour of sulphur in the filter. When the oxidizing power of the bed has been exhausted, it is regenerated with permanganate, then backwashed with water to remove the collected sulphur.

The dose of permanganate has critical limits. If reducing substances such as H_2S are present, deactivation of the filter medium would gradually result. Overtreatment eventually results in pink effluent from the filter bed.

This oxidation process also destroys bacteria and viruses in much the same manner as oxidation with chlorine. The oxidation and bactericidal effect of permanganate does not however, continue through the filter.

Thus, a water which has received permanganate treatment before filtration, although such treatment is applied to the filter with little if any chlorine demand, may require post-chlorination to the desired residual.

APPENDIX A



APPENDIX A

Department of Energy, Mines and Resources
Ministère de l'Énergie, des Mines et des Ressources

Inland Waters Branch
Direction des eaux intérieures

File Number
N° à rappeler

Hydrologic Sciences Division,
J. D. Keys, Chief.

O t t a w a,
January 21, 1969.

Mr. A. V. Giffen,
Division of Research,
Ontario Water Resources Commission,
801 Bay Street,
Toronto 5, Ontario.

Dear Mr. Giffen:

Re: Removal of H₂S from Groundwater

Thank you for the manuscript by A. Oda and for your explanation of the various problems involving the removal of H₂S from groundwater.

My statement to Mr. A. Mellary in my letter dated December 4, 1968, was a general one and I would like to elaborate on it now.

Last summer, I visited more than 2,500 homes (farms) in Russell County gathering well information for a hydrogeological study. I also realized that the general public never quite understands why these scientific or practical studies are carried out by various government agencies. Of these 2,500 homes, some 500 (20%) reported having H₂S in their groundwater supply, and about as many did not report any H₂S in their water supply for various reasons. Consequently, I thought that some work could be done either by O.W.R.C. or by ourselves (E.M.R.) to get rid of H₂S in the groundwater supply of these individual farm houses. (I had no municipal supplies in mind at all.) If this was feasible, then the inhabitants of the region would be made aware that the study or studies carried out were not done in vain.

What I had in mind was to carry out a simple experiment in the field and observe the results. I know others have studied the matter as shown by the report of A. Oda, nevertheless, I firmly believe an experiment using the aeration method should be carried out. The set up would have to be of low cost and kept as simple as possible so that a farmer could incorporate it in his present supply system.

Mr. A. V. Giffen

January 21, 1969

Now what I would like to know is this, is your Division or some division of O.W.R.C. interested in doing this? Or should we (E.M.R.) carry out the experiment? As for data on the wells of the region, I am well supplied. Most farms have pressure systems. The average daily use is less than 500 gpd (domestic supply). The pH is between 7.0 and 8.6. The H₂S concentration varies from 0.1 to 5.0 ppm. (minimum and maximum range of Hack Kit analysis). The hardness of the water is less than 100 ppm.

I have chosen a site (school well), Lot No.8, Conc XI, Cumberland TWP, Russell County, where the experiment could be carried out. All I require is the School Board's approval, and that should not be difficult to get. The test or experiment could be carried out during the summer holidays.

If our experiment proved successful, it could very easily be publicized in the region concerned and, as mentioned before, it would help change the opinion that we are just driving around in government vehicles as some believe at the present time.

This, then, is my proposal. I would appreciate any comments that you might like to make on it.

Yours sincerely,

A handwritten signature in cursive script, reading "J. E. Charron", followed by three asterisks (***) to the right.

J. E. Charron,
Groundwater Subdivision.

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APPENDIX B

B: AERATION

Aeration is the intimate mixture of air into water with the subsequent release of dissolved gases and their replacement with oxygen by absorption. Depending on the pH value of the raw water, aeration may be used to remove or reduce concentrations of H_2S causing odour.

Powell (1) has studied the removal of H_2S from well water by forced-draft aeration and by combined pH reduction and aeration. The well water had a pH of 7.7, an alkalinity (HCO_3) of 205 ppm, a sulphide content (expressed as H_2S) of 17.8 ppm, and a temperature of $54^{\circ}F$. The average air temperature was $70^{\circ}F$. Preliminary data established during earlier work were used initially in these studies - that is, 7.5 cfm of air per gpm of water and 15 gpm per square foot of cross-sectional area. The preliminary data also set the height of the aerator at 16 feet.

Forced-Draft Aeration

The data developed by Powell (Table B.1) indicates that the total sulphides, expressed as H_2S , can be reduced, without decreasing the pH, to almost 1 ppm by forced-draft aeration provided the flow rates are sufficiently low. This

operation requires considerable cross-sectional area, however, necessitating extremely large apparatus. Also, as previously mentioned, concentrations of sulphides from 5 to 20 ppm are extremely objectionable when H_2S is discharged into the atmosphere as a result of aeration.

Additional data illustrates the effect air flow per unit of water has in reducing the sulphide concentration. Beginning with an air flow of 2 cfm per gpm and increasing progressively to 10.4 cfm, it was noted that the total sulphide could not be reduced below 9 ppm. During these tests, the water flow was maintained constant at 15 gpm per square foot of area. It was concluded from these results that, with the normal pH of the well water (7.7), excessive air flows are not effective in reducing the sulphide residuals, provided the cross-sectional area is constant.

Combined pH Reduction and Aeration

When the pH value of the water supply is above 7.0 the sulphides are mostly present as metallic salts. Thus, the "release rate" of sulphides from the water will be slow. Powell, reporting on work by Pomeroy, calculated the theoretical "release rates" for H_2S and recorded the predicted volume of

sulphide that could be removed by aeration at different pH values (Table B.2). In the same table, experimental results obtained on reducing the pH prior to forced-draft aeration have been recorded with the theoretical results. The conditions for these data were: water flow, 15 gpm per square foot of area; air flow, 7.5 cfm per gpm; water temperature 54°F; and air temperature, 70°F. The influent pH was reduced from 7.7 to 2.0 by the application of 10 percent sulphuric acid (H_2SO_4). As the data indicates, additional reduction was effected by lowering the pH value compared to aeration only (Table B.1). The effective point for H_2S removal is between pH values of 4 and 5. Below this point it is apparent that appreciable reduction in pH to approach a zero residual of sulphides cannot be brought about readily.

TABLE B.1

H₂S Removal by Forced-Draft Aeration

<u>Water Flow</u> <u>gpm per sq ft</u>	<u>Residual H₂S</u> <u>ppm</u>
3.4	1.3
4.0	1.6
4.5	2.0
6.0	3.1
15.0	9.0

TABLE B.2

H₂S Release Rates at Different pH Values

<u>Influent pH</u>	<u>Residual H₂S, ppm</u>		<u>Effluent pH</u>
	<u>Theoretical</u>	<u>Actual</u>	
2	NA*	1.7	2.
4	NA	1.7	4.3
5	0.3	2.1	5.4
6	2.	2.8	6.5
7	8.	4.4	7.6
7.5	NA	6.0	8.3
7.7	NA	9.0	8.6

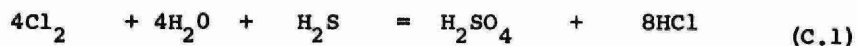
* NA - no analysis

APPENDIX C

C-1: CHLORINATION

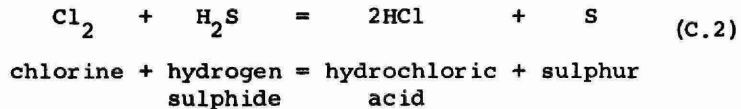
Although well water containing concentrations of H_2S can be treated by aeration, this method does not completely remove H_2S nor does it readily lend itself to the treatment of small farm water supplies. If it is desired to reduce the sulphide level to zero, chemical treatment is required, regardless of whether aeration alone or a combination of pH reduction and aeration is used.

Complete removal of low concentrations of H_2S from well water can be best accomplished by means of chlorination. Chlorine is a strong oxidizing agent, which when present in water as free available chlorine, will oxidize the sulphides to less objectionable forms. Powell has conducted chlorine removal tests with a water having a pH of 7.8 and a temperature of $57^{\circ}F$. The results for removing sulphide residuals in a concentration of from 0.5 to 10.0 ppm of H_2S are shown in Table C.1. The theoretical results recorded in the table are based on the reaction:



Chlorine + water + hydrogen sulphide = sulphuric acid + hydrochloric acid

The discrepancy between the theoretical and actual results is probably due to the precipitation of sulphur, according to the reaction:



In this reaction, theoretically 2.1 pounds of chlorine are required for the removal of each pound (10.5 cu ft) of H_2S , whereas in equation (C.1) the theoretical requirement is 8.4 pounds of chlorine.

Treatment

If the sulphide content of the well water is constant without fluctuations in concentration, the chlorine feed ratio can be set to produce the desired free chlorine residual, normally 1 ppm. (Residual chlorine test kits may be obtained from one of the Public Health Laboratories of the Ontario Department of Health.) Figure C.1 is a schematic diagram of a suggested method for the feeding of chlorine. The chemical feeder is installed in conjunction with the pressure system; when the well pump is in operation, the chemical feeder draws the chlorine solution (2 percent chlorine by weight) from a chlorine-resistant container and feeds a controlled amount into the water, preferably down the well at the end of the

pump drop pipe. The chlorine oxidizes the H_2S eliminating the bad odour and corrosion problems, and also kills any sulphur bacteria present. The chlorine solution may be prepared using commercial bleach which is available at most agricultural supply houses. Ordinary household laundry bleach (sodium hypochlorite) may be substituted, however, this would increase the cost.

Sometimes, the H_2S level may not remain nearly constant but will fluctuate over a wide range of concentrations. To ensure complete oxidation of the sulphides and to allow for variations in H_2S which may occur in the water supply, the chemical feeder is usually set to maintain a reasonably high chlorine residual in the treated water. Because the addition of an excess of chlorine reduces the contact time required, the chlorine may be added at the pump. Following chlorination, the water for most purposes is passed through a sediment filter to remove the precipitated sulphur. To remove the objectionable chlorine taste and odour, a large carbon filter should be installed after the sediment filter to dechlorinate the whole water supply. Generally, the smaller cartridge-type activated carbon filters do not have the capacity to remove large quantities of chlorine (Figure C.2).

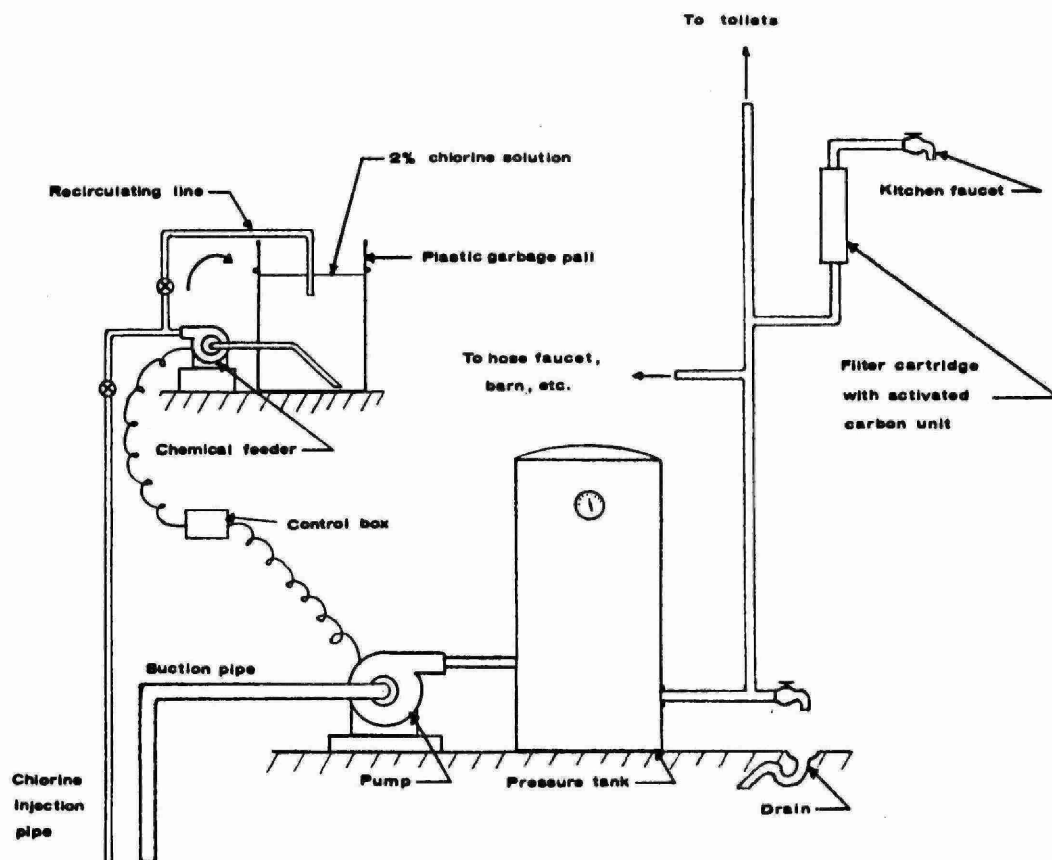


Figure C.1 Schematic Arrangement of Chlorinator for H_2S Removal.

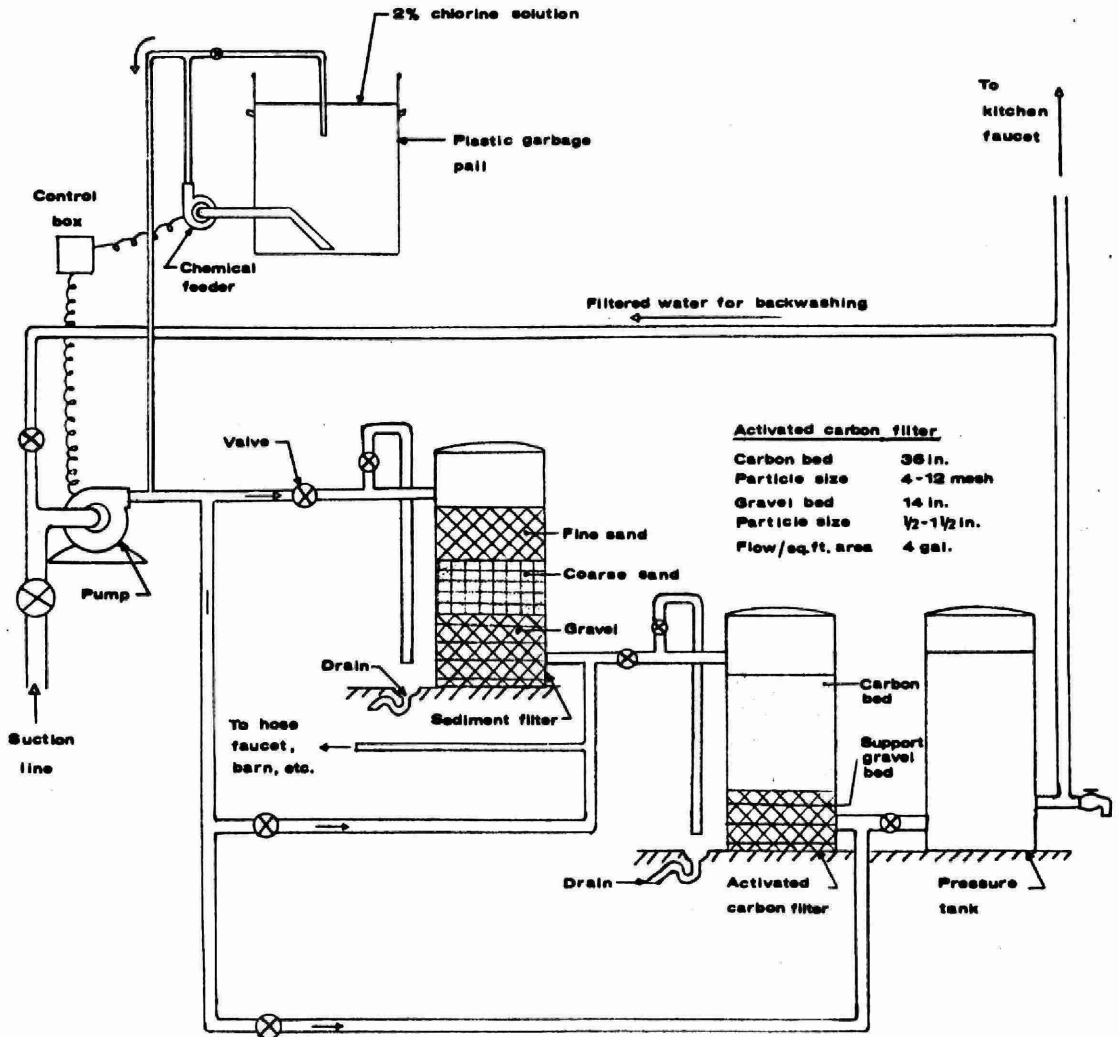


Figure C.2. Schematic Diagram Showing Chlorination - Filtration - Dechlorination Treatment for H_2S Removal.

TABLE C.1

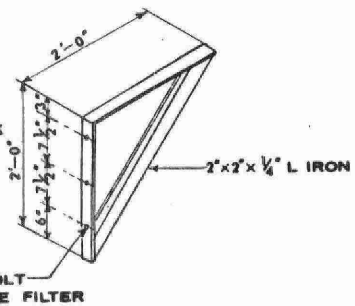
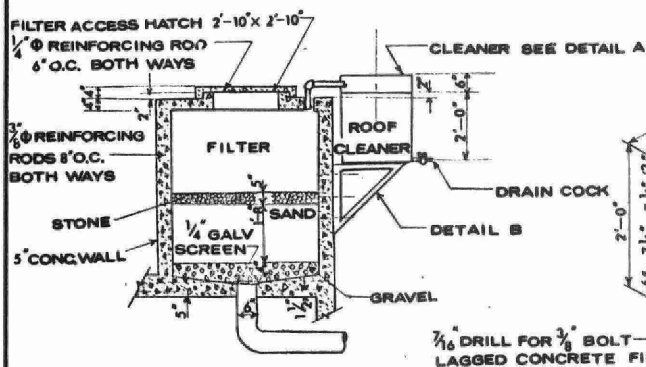
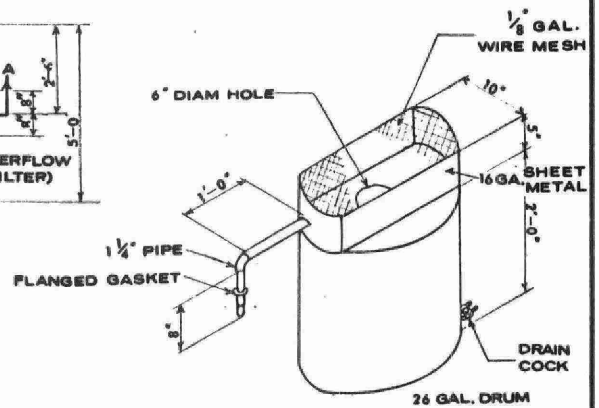
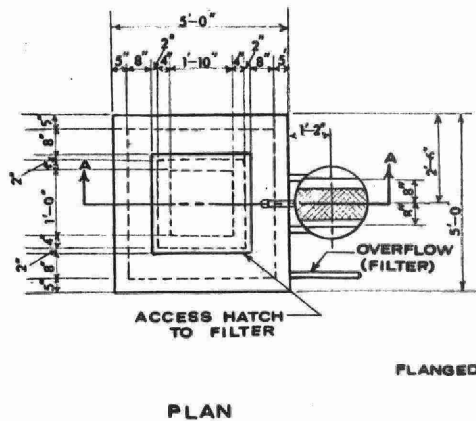
Actual and Theoretical Results of H_2S Removal by Chlorination

Sulphide Concentration <u>ppm H_2S</u>	Chlorine Demand, ppm	
	<u>Theoretical</u>	<u>Measured</u>
0.5	4.2	2.
1.	8.4	6.
2.	16.8	15.
4.	33.6	30.
6.	50.4	45.
8.	67.2	61.
10.	84.0	76.

C-2: SEDIMENT REMOVAL

Commercial filters are available to remove sediment from water. These filters are made of different types of porous material or sand and gravel. The porous material types are usually molded units manufactured to fit into a cartridge which directs the flow through the filter. The filter element is easily removed for replacement or cleaning. The sand and gravel filter consists of a tank filled with layers of fine sand, coarse sand and gravel. It is equipped with valves so that the filter may be backwashed as required to keep it effective and sanitary.

Construction details for a homemade filter to be used with a cistern are shown on Plan No. A158-8083 of the Canadian Farm Builder Plan Service (Figure C.3).⁽⁶⁾



FILTER CHARGE

GRAVEL ----- $\frac{1}{3}$ cu. yd.
SAND ----- 1 cu. yd.
STONE ----- $\frac{1}{3}$ cu. yd.

ONTARIO WATER RESOURCES COMMISSION
DIVISION of RESEARCH

CONSTRUCTION DETAILS

HOME MADE SEDIMENT FILTER

COURTESY CANADIAN FARM BUILDING PLAN
SERVICE

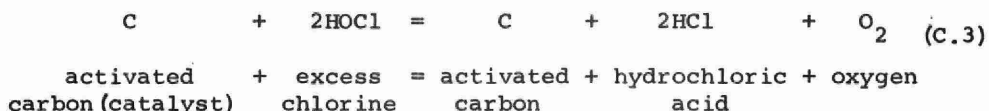
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FIGURE C.3

C-3: ACTIVATED CARBON FILTER

Activated carbon is the best material for complete removal of chlorine taste and odour. Even if the concentration is higher than 6 ppm, the chlorine is completely removed. Regeneration is generally unnecessary because the chlorine is not actually adsorbed but is oxidized to hydrochloric acid (HCl) as a result of the catalytic effect of the carbon (Equation C.3).



Well water will generally have enough carbonate to neutralize the HCl generated.

Carbon filters are available as a small replaceable molded unit which fits inside a cartridge or as a large bed of granular carbon contained in a tank similar in appearance to a softener (Figure C.4). Water containing sediment should be passed through a sediment filter prior to entering a carbon filter because the sediment will rapidly coat the carbon granules, causing premature reduction in its capacity to remove taste and odour.⁽⁴⁾

With the larger filters, the carbon layer should be at least 36 inches thick and the filter containing it

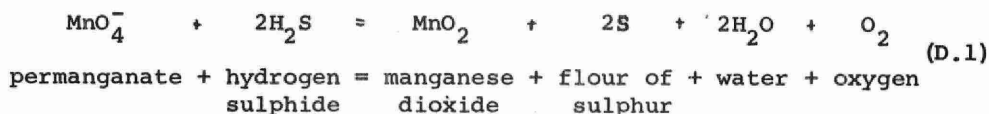
designed to insure complete distribution of the water. The carbon should be washed once every 14 days by use of a counter-flow of filtered water. Additional design data is given in Figure C.2.

APPENDIX D

D: POTASSIUM PERMANGANATE

KMnO_4 may be effectively used to remove concentrations of H_2S below 2.5 ppm. Above this level either chlorination-filtration or aeration-chlorination-filtration should be used.

Small chemical feeders which automatically feed a KMnO_4 solution (1 percent KMnO_4) into the water are available commercially. A schematic diagram showing a suggested feed system is illustrated in Figure D.1. When the water pump is in operation, the solution feeder automatically draws the permanganate solution from a mixing tank and feeds a controlled amount into the water line. The automatic feeder is adjusted by gradually increasing the dosage until a sample of water from the sample probe just above the filter bed shows a very slight pink permanganate colour (indicates 0.05 ppm excess permanganate). The permanganate oxidizes the H_2S to flour of sulphur, according to the reaction:



To remove the slight pink colour and to collect the precipitated sulphur, the treated water is passed through a manganese green sand filter. The green sand filter media catalyzes the excess MnO_4^- and lower oxides to MnO_2 and acts

like a sand filter to remove the precipitated sulphur.

Periodically, the unit must be regenerated with permanganate solution then backwashed with water to remove the collected sulphur.

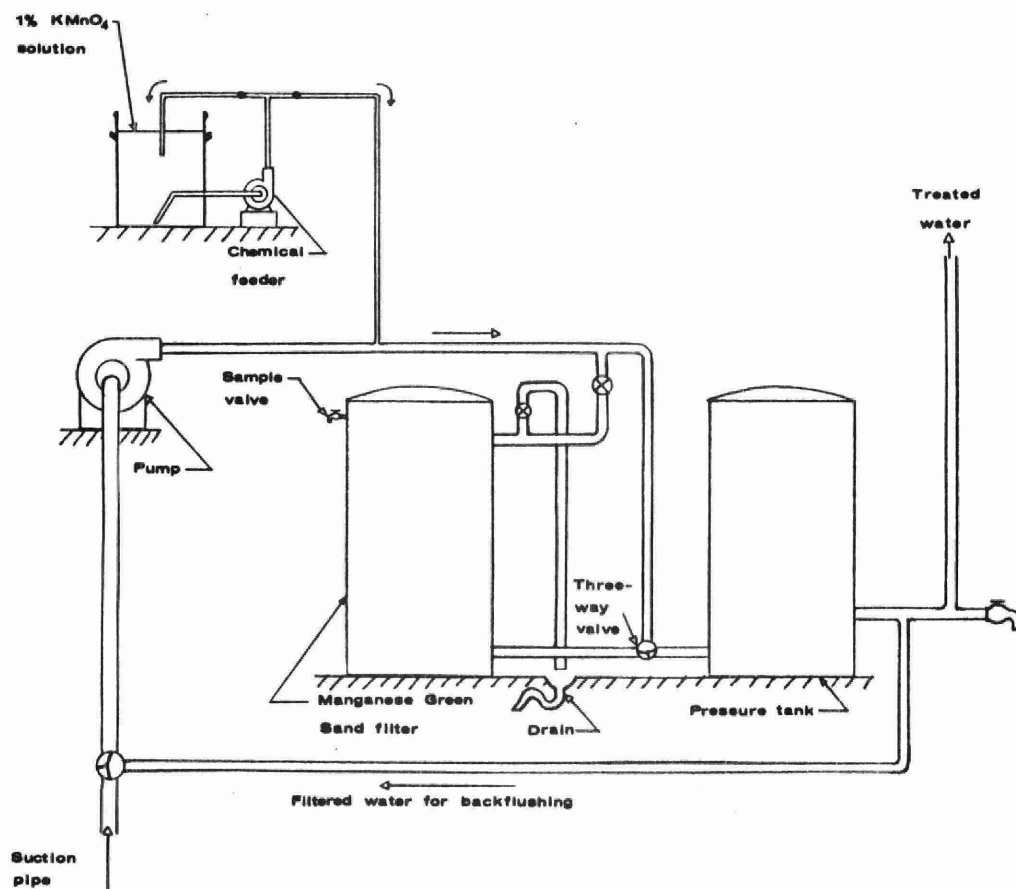


Figure D.1. Schematic Diagram Showing $KMnO_4$ Treatment for H_2S Removal.

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